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(12) UK Patent Application (19) GB (11) 2 187 096 (13) A

(43) Application published 3 Sep 1987

(21) Application No 8704524

(22) Date of filing 26 Feb 1987

(30) Priority data

(31) 8600888 (32) 27 Feb 1986 (33) SE

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(51) INT CL[4]
A01N 37/02 59/20

(52) Domestic classification (Edition I)
A5E 108 228 232 247 274 279 BB
U1S 1306 A5E

(56) Documents cited
US 4335109

(58) Field of search
A5E
Selected US specifications from IPC sub-class A01N

(54) **Preservative for wood**

(57) Wood or other organic fibrous material is preserved by treating it with copper acetate in solution and zinc acetate in solution; the copper acetate amounting to at least 45%, preferably 60 to 90% and more preferably 75 to 85%, by weight of the total amount of copper acetate and zinc acetate applied. The copper and zinc acetate may be applied together in one solution.

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SPECIFICATION

Preservative for Wood

The present invention represents a further development of the preservative for wood and other fibrous material described in my Swedish patent 430.865.

For much more than a century aqueous solutions of copper sulphate and zinc chloride have been used as wood preservatives. These salts have given a good protection. They have, however, had certain disadvantages. Copper sulphate attacks iron instantaneously and can therefore not be used in ordinary pressure plants, further it has in some special cases a weak preservative effect. The zinc chloride also acts as a corrosive but in another way, in addition its preservative effect is not so high. For such reasons these preservatives have been replaced by other salt preservatives in which copper and zinc compounds are often present as important ingredients.

The salts have, in spite of their solubility, provided good protection. This may be because the preserving ingredients, copper and zinc, to a certain extent are fixed in the wood. In order to obtain information about this some leaching tests have been carried out. Wood blocks of pine sap wood with a volume of 15 cm^3 were fullcell impregnated with different strong solutions of copper sulphate and zinc chloride respectively. After drying the blocks were leached in running water for 30 days whereafter remaining amounts of copper or zinc were estimated. The results were as follows.

TABLE 1

Per Cent Cu or Zn in Solutions of Copper Sulphate and Zinc Chloride Respectively	Remaining Amounts after Leaching of Cu or Zn in Per Cent of Introduced Amounts of Cu or Zn	
	Cu	Zn
0.1	58	45
0.2	49	33
0.3	42	27
0.4	36	24
0.5	32	19
0.7	27	14
1.0	21	10
1.2	19	9

An amount of 0.1 (0.2, 0.3 etc.) in the table corresponds to 0.393 per cent $CuSO_4 \cdot 5aq$ (=0.1 per cent Cu) or, when zinc is concerned, to 0.208 per cent $ZnCl_2$ (=0.1 per cent Zn) etc.

In this specification, concentrations of solutes in solution are expressed as weight/volume percentages and other percentages are expressed by weight.

If these sulphates and chlorides are replaced by copper or zinc acetates an improved fixation is obtained. For low contents the fixation is almost complete but at all concentrations is to some degree better for copper than for zinc. For copper acetate solutions containing 0.3 per cent copper or more, in general, twice as much copper is fixed as for copper sulphate solutions. After impregnation with an acetate solution containing 0.3 per cent copper, in a short time, up to 85 per cent of the copper is fixed, if the solution contains 0.6 percent copper up to 64 percent is fixed and if the solution contains 1.0 per cent copper, 48 per cent is fixed. By use of zinc acetate instead of zinc chloride a corresponding improved fixation is achieved.

As said above zinc compounds are not fixed to the same degree as copper compounds. At low concentrations values for zinc are obtained which are close to the results which are obtained for copper. At higher concentrations zinc compounds are, as a rule, fixed only half as well as copper compounds.

Further it is interesting to observe that the amount of zinc which the wood can fix is surprisingly invariable within a wide range of concentrations. From the above leaching results for zinc chloride it is evident that the remaining amount of zinc in wood after leaching increases with increased introduced amount of zinc chloride up to zinc contents of 0.3 to 0.4 per cent. Thereafter the degree of the fixation decreases to about the same extent as the concentration of the solution increases. The remaining zinc, after leaching will, in a wide concentration range be about the same and roughly independent of the amount of zinc chloride introduced into the wood. If the solution contains 0.3 per cent zinc, 27 per cent of this content is fixed according to the Table 1 above. As a relative measure of the remaining amount of zinc after leaching the figure 0.081 (27% of 0.3=0.081) can be given. If the solution contains 0.4 per cent zinc 24% is fixed which

gives the comparison figure 0.096. If a 1.2 per cent zinc solution is introduced, 9 per cent is fixed and the figure will be 0.108. If the content of zinc in the solution is quadrupled—increased by 400 percent—that is increased from 0.3 to 1.2 per cent the protecting amount left after leaching is increased only from 0.081 to 0.108, that is by 33 per cent. If the zinc content is tripled—increased by 300 per cent—that is increased from 0.4 to 1.2 per cent, the protecting amount is increased from 0.096 to 0.108, that is 12 per cent. From this it follows that there is not much reason to use solutions of zinc chloride containing over 0.3 to 0.4 per cent zinc. The fixation of the zinc is considerably increased if acetate is used instead of chloride but on the other hand the fixation of the zinc acetate diminishes when it is used—as the intention is here—in combination with higher amounts of copper acetate.

The amount of preservative per amount of wood has been given above in the form of a concentration of a solution which has been introduced in the wood by a full cell treatment. To use full cell treatment when carrying out experiments is common and scientific as hereby a uniform distribution of the preservative in the wood is obtained which is hardly possible if stronger solutions and treating methods with smaller amounts of solution are used.

The fixation of the described preservative has a close connection with the amount of preservative introduced per weight amount of wood. Low amounts of preservative are better fixed than higher amounts. This is an advantage over the opposite which as a rule prevails for most negative preserving radicals.

If some parts of the wood should receive so high an amount of preservative that a part remains unfixed the surplus can diffuse and be fixed in the parts of the wood that at the time of treatment have received less preservative. This situation is common because in practical preservation the outer parts of the wood always get more preservatives than the inner parts. The properties of the preservative help to transport preservative from the wood that has received more preservative to the part that has received less, which part, as a rule, is more exposed to wood destroyers. In this way a more uniform distribution and a more effective protection of the wood is obtained.

Further the acetates have a tendency in the long run to decompose in the wood with evaporation of free acetic acid the remaining metal having improved fixation.

Copper salts give excellent protection against decay. Unfortunately there are a few fungi that are resistant to copper. These can rapidly destroy the wood and cause incalculable and troublesome damage. These are well known facts, they have been made clear by tests with fungi, field tests and practical experience.

In Wood Preservation 1978 by Richardson, page 133, there is written "The main problem with all copper preservatives has been that some fungi are resistant to them". More detailed information in these respects is given for example in "Wood Preservation during the last 50 years" and in "Holzkonservierung".

Zinc has as above indicated a lower protecting effect than copper. It is difficult to give a quantitative relationship as the kind of decay attacks varies. It may, however, be possible to say that copper has at least four times the preserving effect of zinc. The zinc has, however, a greater all round effect. In the particular cases when copper alone has a low effect the zinc in combination with copper gives excellent complementary preserving protection in which a synergetic effect is included. With respect to the lower common effect and to the lower fixation of the zinc compounds they ought to be used only in a limited amount and in order to complement the effect of the copper.

Investigations in the laboratory—such as "agar" tests—show that the effect of the preservative against copper resistant fungi seems to be sufficient if the zinc acetate reaches 10 to 15 per cent of the total amount of acetate in the preservative. In these investigations no leaching has been carried out. With regard to the lower leaching resistance for zinc than for copper the zinc content may be increased over the given figures up to a suitable value of 25 per cent, there is no reason to increase it over 50 to 55 per cent. Field tests have confirmed this, an extensive one is described below.

For obtaining the best result it is evident that the copper acetate content ought to be high and zinc acetate must be present but in a limited amount. Sharp limits can not be defined. The content of copper acetate ought to be higher than 45 to 50 per cent, preferably over 60 per cent, most suitable seems to be around 75 per cent of the total amount of metal acetate. The content of the copper acetate may not exceed 85 to 90 per cent as in such cases the effect from the zinc will be too low.

Earlier preservatives containing copper and zinc salts have been based on a higher amount of zinc and a lower amount of copper. In the United States of America there exists a well known preservative, chromated copperized zinc chloride, in which the active compounds zinc chloride and copper chloride are present in proportions of about 10 to 1.

In Swedish patent No. 430.865 there are also disclosed mixtures of zinc and copper salts where similarly it is presupposed that the zinc salt has to be present in predominant amount. In the example given the zinc salt is present in five times as high an amount as the copper salt.

Further, boric acid (H_3BO_3) may be included in the preservative. It can hasten the decomposition of the acetates and support the fixation of the metal radicals. Further the boric acid contributes to the protection of the wood against mould and blue stain during the drying after impregnation. Even if boron has a high preserving effect there is no reason to use an higher content which in the past has been the rule. Boron compounds will not be effectively fixed; they are leached out quickly to begin with, then more and more slowly. Further a high content of boric acid can reduce the leaching resistance of the metal radicals. The content of boric acid may be limited to 5 to 10 per cent of the weight of the metal acetates.

A deciding advantage with the described acetate preservative is that the corrosion by iron can be kept under control. The purer the chemicals, the lower the content of chlorine etc., the less is the corrosion. Reduced corrosion is also achieved if the solutions are not too acid. With small amounts of ammonia or ammonium salts, or alkali or alkaline salts this can be kept under control. Addition of one or some hundredths of a per cent of sodium nitrite is very effective. A good effect has also been obtained by addition of some hundredths of a per cent ammonium acetate.

Before the crucial field test is described it may be said that copper acetate has been field tested for many years. A good average durability of the wood has been achieved but occasionally decay damage has occurred which can not be tolerated. It has been pointed out above that copper preservatives have such properties, these facts are well known.

The following test to ascertain the effect of boric acid was carried out. In an eight year field test on three fields three different copper preservatives were tested, one solution contained 0.3 per cent copper as the only preservative agent, the second solution contained 0.3 per cent copper and 0.15 boric acid, the third one contained 0.3 copper and 0.30 boric acid. The average decay index (the term is explained below) for the three preservatives at the three fields were after eight years 25.7 25.8 and 28.3. It is clear that the boric acid—dependent on leaching—had no real effect.

The preservative according to the invention has been investigated in extensive field tests. One of them is of special interest. It was started in 1981, and carried out under impartial official management according to standardized norms. The preservative had the composition:

Copper acetate	$CuAc_2 \cdot aq$	73 per cent by weight = ≤ 25% Cu
Zinc acetate	$ZnAc_2 \cdot aq$	23 per cent by weight
Boric acid	H_3BO_3	4 per cent by weight

Pine wood stakes with exact dimensions were fullcell treated with solutions containing 0.7, 0.9, 1.3, 1.8 and 2.6 per cent of this preservative. 20 stakes were impregnated with each concentration and after storing and drying were placed in the ground in the field to half their length. As a comparison stakes treated with a solution of 1.8 per cent of the preservative K33 based on copper, chromium and arsenic compound (see my Swedish Patent 139.177) were placed in the field. This preservative is used in around 60 countries and is considered the most effective obtainable. Of course untreated stakes were also placed in the field for comparison. Every year all stakes are inspected and the extent of their decay is calculated; the average extent of decay is given in form of a decay index. If no damage can be observed on any stake in the series the decay index is 0, if all the stakes in the series are quite decayed in the ground line the decay index is 100.

The tests are carried out on two test field, one—Simlångdalen—with extreme decay intensity, a second—Tåstrup—with more normal conditions.

At the inspection after 5 years the stakes that had been treated with the preservative according to the present invention—marked CZB—had the following decay index.

Preservative	Concentration of Solution	Decay Index Simlångdalen	Tåstrup
CZB	0.7	39	8
	0.9	34	5
	1.3	13	0
	1.8	3	0
	2.6	0	0
K33	1.8	6	5
Untreated stakes		100	100

The decayed untreated stakes had at Simlångdalen an average durability of 1 year, at Tåstrup of 2.9 years.

From the table it appears that in Simlångdalen a content between 1.3 and 1.8 percent of CZB gives the same protection as 1.8 per cent K33. In the Tåstrup field 0.9 per cent has given the same protection as 1.8 per cent K33. The CZB salt thus has a much higher effect than K33.

In order to show that the ingredients and their proportions have a deciding importance for the effect of the preservative a further test was carried out using a preservative "ZB", as a comparative example. ZB

contains zinc acetate and a small amount of boric acid. The same test as for the preservative CZB was carried out. The following results were produced by the 5 years inspection.

Preservative	Concentration of Solution	Decay Index Simlångdalen	Tåstrup
ZB	1.1	89	90
	1.6	79	95
	2.2	78	73
	3.1	36	53
	4.4	19	45

The preserving effect of CZB is thus higher than for ZB. The results as Simlångdalen show that 0.7—0.9 per cent CZB gives the same protection as 3.1 per cent of ZB and that 0.7 per cent of CZB at Tåstrup gives a far better effect than 4.4 per cent of ZB. From this it is clear that CZB has several times as high an effect as ZB. This in accordance with the above information that zinc has four times lower an effect than copper and that this effect is further reduced by leaching.

The test result is unique. K33 was developed almost 40 years ago and has been unsurpassed ever since. Now a new preservative—CZB—over long field tests—has shown a higher effect, it can thus be used in a lower quantity. There is, more importantly, the environmental advantage of CZB over K33 to consider: the preservative CZB contains, in contrast to K33, neither chromium nor arsenic. For a long time many attempts have been made to develop such a preservative; but up to now chromium and arsenic free preservatives have had a much lower effect.

The preservative is generally used in water solution in the concentrations given in the above related tests, that is in about 1 to 2 per cent. Such solutions are used for ordinary fullcell treatment of Swedish pine which as a rule absorbs 300 litres of solution per cubic metre. For the treatment of wood to be used in sea water where Teredo occurs, as a rule 3 to 4 per cent solution is used. By the Lowry treatment about half the amount of solution is introduced into the wood as when fullcell treatment is used. When Lowry treatment is used, therefore, the strength of the solution has to be adapted to this fact, as a rule for Lowry treatment 2 to 4 per cent solution is used in order to apply to the wood the desired amount of preservative.

Although in the tests described above the copper and zinc acetates were applied simultaneously and in one solution, it is envisaged that the solutions could be applied separately, one after the other.

CLAIMS

1. A mixture for preparing a preservative solution for wood and other organic fibrous materials which comprises copper acetate and zinc acetate and where the content of the copper acetate amounts to at least 45% by weight of the total content of copper acetate and zinc acetate.

2. A mixture as claimed in claim 1 wherein the copper acetate content is from 60% to 90% by weight of the total content of copper acetate and zinc acetate.

3. A mixture as claimed in claim 2 wherein the copper acetate content is from 75% to 85% by weight of the total content of copper acetate and zinc acetate.

4. A mixture as claimed in any one of the preceding claims which comprises boric acid (H_3BO_3) as an additive in a concentration not exceeding 10% by weight based on the amount of copper acetate and zinc acetate.

5. A mixture as claimed in claim 4 wherein the boric acid concentration does not exceed 5% by weight based on the amount of copper acetate and zinc acetate.

6. A mixture as claimed in any one of the preceding claims which comprises an alkali or alkaline salt or ammonia or ammonium salt as an additive in a concentration not exceeding 0.1% by weight based on the amount of copper and zinc acetates.

7. A mixture as claimed in claim 6 wherein the additive is an alkaline or ammonium nitrite or acetate.

8. A preservative solution for wood and other organic fibrous materials, which comprises copper acetate and zinc acetate and where the copper acetate content amounts to at least 45% by weight of the total content of copper acetate and zinc acetate.

9. A preservative solution as claimed in claim 8, wherein the concentration of copper and zinc acetates and optionally additives are as defined in any one of claims 2 to 7.

10. A preservative solution as claimed in claim 8 or claim 9 wherein the total concentration of copper and zinc acetates and any additives in solution is from 0.5 to 4% W/V.

11. A preservative solution as claimed in claim 10 wherein the total concentration of copper and zinc acetates and any additives in solution is from 1 to 2% W/V.

12. A method of treating wood or other organic fibrous material to preserve it, which comprises treating the wood or other material with copper acetate in solution and zinc acetate in solution, and where the

copper acetate amounts to at least 45% by weight of the total amount of copper acetate and zinc acetate applied.

13. A method as claimed in claim 12 wherein the amount of copper acetate applied is from 60 to 90% by weight of the total amount of copper acetate and zinc acetate applied.

14. A method as claimed in claim 13 wherein the amount of copper acetate applied is from 75 to 85% by weight of the total amount of copper acetate and zinc acetate applied.

15. A method as claimed in any one of claims 12 to 14, which comprises treating the wood or other material with boric acid (H_3BO_3) in solution as an additive and where the amount of boric acid applied does not exceed 10% by weight of the total amount of copper acetate and zinc acetate applied.

16. A method as claimed in claim 15 wherein the amount of the boric acid applied does not exceed 5% by weight of the total amount of copper acetate and zinc acetate applied.

17. A method as claimed in any one of claims 12 to 16 which comprises treating the wood or other material with a solution of an alkali or alkaline salt or ammonia or ammonium salt as an additive in an amount which does not exceed 0.1% by weight of the total amount of copper acetate and zinc acetate applied.

18. A method as claimed in claim 17 wherein the solution is a solution of an alkaline or ammonium nitrite or acetate.

19. A method as claimed in any one of claims 12 to 18 which comprises applying the copper and zinc acetates and any additives together in one solution.

20. The use of a mixture as defined in any one of claims 1 to 7 or of a solution as defined in any one of claims 8 to 11 or of a method as defined in any one of claims 12 to 19 to fix copper and zinc ions in wood or other organic fibrous material.

21. A preservative solution substantially as hereinbefore described other than as prior art.

22. A method as hereinbefore described other than as prior art.

23. A preservative mixture substantially as hereinbefore described other than as a prior art.

Printed for Her Majesty's Stationery Office by Courier Press, Leamington Spa. 9/1987. Demand No. 8991685.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.